

Optimized Geometry, Charge Distributions, Frontier Molecular Orbital Analysis and NLO Efficiency of BIS (4-Methoxyanilinium) Adipate by Quantum Chemical Calculations

V. Siva, A. Shameem, A. Murugan, S. Athimoolam, S. Asath Bahadur

Abstract: In this work, optimized molecular geometry, vibrational and electronic properties of Bis(4-methoxyanilinium) adipate (4MAA) was obtained by Quantum chemical analysis using 6-311++G(d,p) basis sets. The experimental and computation vibrational spectra have been discussed. Experimental spectra of the 4MAA were recorded in the region 4000–400 cm^{-1} . The experimental and computational assignments were found to be in good agreement. FMO energies showed that charge transfer had occurred within the molecule. Mulliken charge distribution of the present compound was studied systematically. Furthermore, the hyperpolarizability calculations were analyzed.

Keywords: Organic, molecular geometry, HOMO-LUMO and NLO

I. INTRODUCTION

Schiff based compounds are generally considered due to their importance in several electro-optical and other technological applications. π -electron conjugation with aromatic structure is essential to exhibit the nonlinear optical (NLO) properties and on this basis the aniline is consider as one the systems for NLO applications.

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This statement is substantiated by many theoretical and experimental works [1,2]. Aniline based compounds have been widely used as starting materials in a vast amount of pharmaceuticals, optoelectronic devices, dyes and other technical applications [3-5]. Charge transfer based organic molecules have been established in past decades to possess more higher order NLO properties compared to the more conventional inorganic compounds. The present work is focused on the molecular structure optimization by Quantum chemical analysis using 6-311++G(d,p) basis sets. The computational calculations using HF and DFT methods have been carried out. Nonlinear optical parameters such as polarizability, first and second order hyperpolarizabilities were calculated. FMOs analysis and charge distribution of the title compound also explained in detail.

II. RESULTS AND DISCUSSION

A. Molecular geometry

The planarity of the structure is confirmed from the torsion angles and these planar molecules are oriented with an angle of 71.03(4) Å to each other. Protonation on the N-site of the cation is confirmed from elongated C-N bond distance [1.456(3) Å]. Most of the optimized structural parameters are slightly higher than the single crystal XRD values [6], due to the computational calculations belong to isolated molecules gases state (Table I). Optimized Structure for the title compound given in Fig. 1 and Fig. 2.

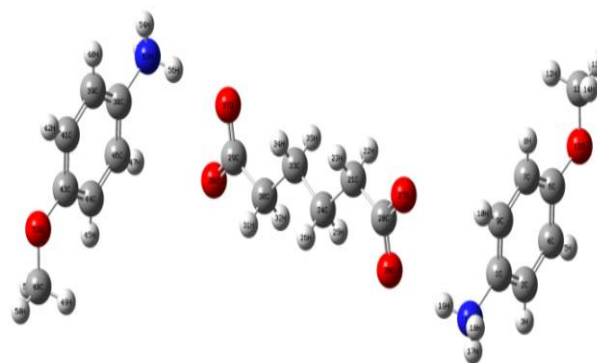


Fig.1. Optimized Structure for DFT/6-311++G(d,p).

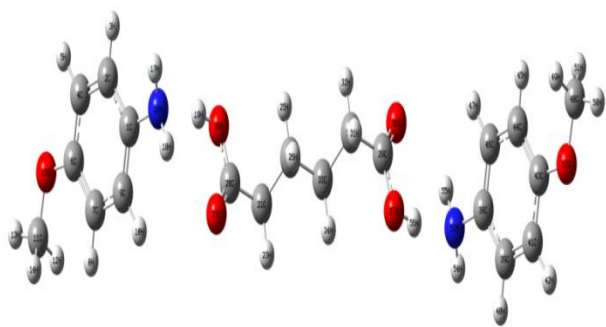


Fig. 2. Optimized Structure for HF/6-311++G(d,p)

B. Mulliken charge distribution analysis

The histogram of atomic charges of 4MAA was shown in Fig. 3. The hydrogen atom (H56) in amine group of 4MAA was more electropositive ($0.684e$ in DFT and $0.408e$ in HF), this hydrogen atom was attached with electronegative atom (N53). Also, oxygen atom has more electro negativity (O27) ($-0.849e$ in DFT and $-0.531e$ in HF), this atom was enclosed by one electronegative oxygen atom (O28) and one carbon atom (C20). The oxygen atoms which are involved in intermolecular hydrogen bending interactions between the anions show electronegative charge values.

C. HOMO-LUMO analysis

FMO analysis of 4MAA are calculated with Gaussian 09W[7] program to calculate the FMO energy gap. The charge transfer of the molecule is also established by the topology of these orbitals and it is shown in Fig. 5. The calculated FMO energy values and other parameters of 4MAA are given in Table 1. Therefore the lowering in the FMO energy gap obviously explains the concluding charge transfer interactions taking place within the molecule and good candidate for NLO applications.

Vibrational analysis

The observed and computed FTIR and FT-Raman spectra are shown in Figs. 6 and 7 and the detailed vibrational assignments (Table II) visualized through Gauss view [7] are discussed below.

Vibration of C-H, C-N, C-C and C=O group

The C-H in-plane bending vibration was observed at 1152 cm^{-1} in IR and well matched with the theoretically counterparts. C-H out of plane bending vibration were calculated at $1010, 1049\text{ cm}^{-1}$ in HF and $936, 953\text{ cm}^{-1}$ in B3LYP methods. The asymmetric stretching of COOH group observed at 1950 cm^{-1} in IR and it is computed at 1959 and 1763 cm^{-1} in the HF and B3LYP levels respectively. Also, the symmetric stretching of COOH group is absent in Raman spectrum. The carboxylic group out-plane bending vibrations is computed at 3158 and 2999 cm^{-1} in the HF and B3LYP levels respectively, but it is absent in experimental IR and Raman spectra. The title compound, 4MAA have the C-N and C=C stretching vibrations occurs in the range $1300\text{--}1600$

cm^{-1} owing to literature. The C=C stretching mode of vibration is observed at 1525 cm^{-1} in IR and computed at 1548 in HF and 1456 cm^{-1} in DFT/B3LYP methods, respectively. The C-N bending mode is observed at 1552 cm^{-1} and 1457 cm^{-1} in HF and DFT/B3LYP methods. This corresponding vibration was absent in experimental spectrum.

Vibration of methyl Group

The stretching vibrations of methyl group were excepted in the range $3010\text{--}2900\text{ cm}^{-1}$. In the present study, the asymmetric stretching vibrational mode is found at the frequency of 3255 cm^{-1} in FT-IR spectrum. In HF and DFT/B3LYP calculation, the CH_3 asymmetric stretching vibration is identified at 3279 and 3131 cm^{-1} respectively whereas in Raman spectrum it is absent. The CH_3 scissoring vibration was observed at 1631 and 1506 cm^{-1} in HF and DFT/B3LYP methods, respectively. The same vibration was observed around 1635 cm^{-1} in IR spectrum and absent in Raman spectrum. The CH_3 wagging mode at 1593 cm^{-1} in Raman spectra and agree well with theoretical results at 1587 and 1471 cm^{-1} in HF and DFT/B3LYP methods respectively. The rocking vibration was observed around 1620 and 1492 cm^{-1} in HF and DFT/B3LYP methods, respectively. Experimental spectra are absent for these vibrations.

Table I: Optimized molecular geometrical parameters for 4MAA

Atom Connected	Experimental	HF/	B3LYP
<i>Bond length (Å)</i>			
C1-C2	1.380(4)	1.393	1.380
C1-C9	1.361(4)	1.380	1.361
C1-N16	1.456(3)	1.418	1.456
C2-H3	0.93	1.077	0.930
C1-C4	1.376(4)	1.377	1.380
C4-H5	0.93	1.075	0.930
C4-C6	1.382(4)	1.392	1.382
C6-C7	1.380(4)	1.382	1.380
C11-O15	1.404(4)	1.397	1.404
C20-C21	1.508(3)	1.507	1.508
C20-O27	1.252(3)	1.191	1.252
C20-O28	1.260(3)	1.317	1.260
C21-H22	0.97	1.086	0.970
C21-H23	0.97	1.083	0.970
C21-C24	1.518(4)	1.530	1.523
C24-H25	0.97	1.086	0.970
C24-H26	0.97	1.088	0.970
C24-C33	1.523(3)	1.528	1.518
<i>Bond Angle (°)</i>			
C2-C1-C9	119.9(2)	118.391	119.947
C2-C1-N16	119.8(2)	120.490	119.805
C9-C1-N16	120.2(2)	121.054	120.239
C1-C2-H3	120.4	119.801	120.430
C1-C2-C4	121.2(2)	120.825	119.147
C4-C6-C7	118.7(3)	118.918	118.715
C4-C6-O15	122.8(2)	116.090	116.030
C7-C9-H10	109.4	119.175	119.475
C6-O15-C11	118.2(2)	119.622	118.248
C1-N16-H17	109.5	112.314	109.477
C1-N16-H18	109.5	112.287	109.471
<i>Torsional Angle (°)</i>			
H25-C24-C33-C30	57.5(3)	58.346	59.0529
H25-C24-C33-H34	178.2(2)	179.999	179.997
H26-C24-C33-H35	179.5(1)	180.000	180
H45-C44-C46-C38	178.2(2)	179.920	178.777

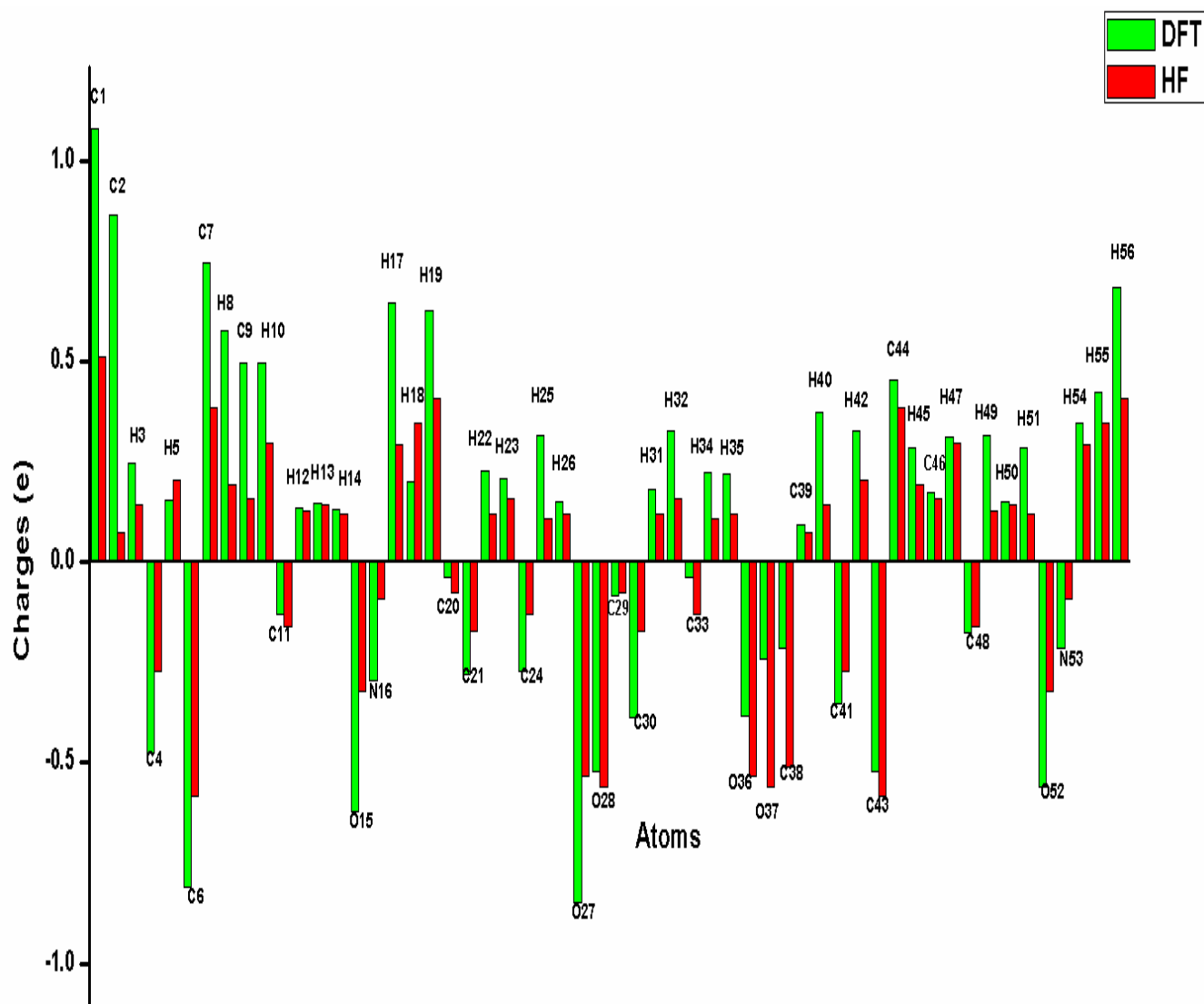


Fig.3. Mulliken charge distributions for 4MAA

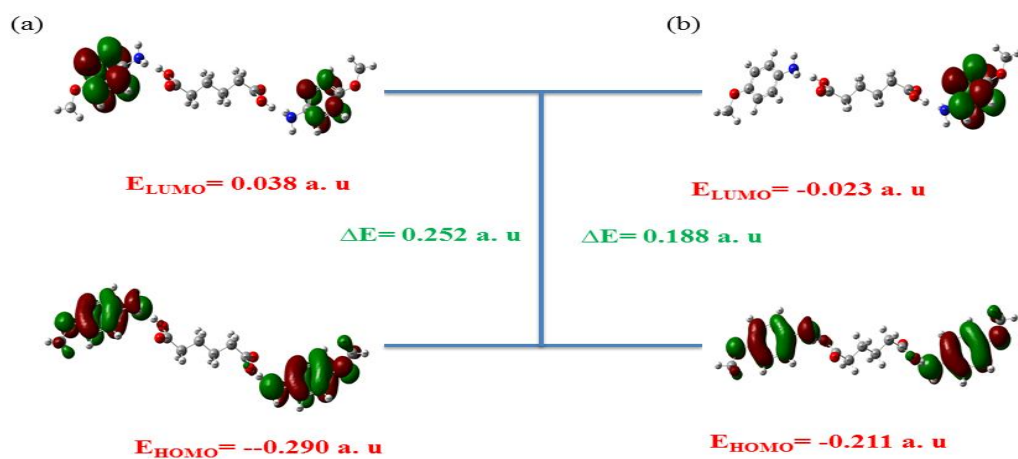


Fig. 4. Molecular orbital energy diagram for 4MAA

Table II: Calculated energy values of 4MAA

Parameters (au)	HF	B3LYP
E_{LUMO}	0.038	-0.023
E_{HOMO}	-0.29	-0.211
$\Delta(E_{LUMO} - E_{HOMO})$	0.252	0.188
Electron Affinity (A)	-0.038	0.023
Ionization Potential (I)	0.291	0.211
Chemical Hardness (η)	0.164	0.094
Electronegativity (χ)	0.126	0.117
Chemical Potential (μ)	-0.126	-0.117
Electrophilicity Index(ω)	0.049	0.073

Table III: Vibrational Assignments of 4MAA

Mode Number	Experimental		HF/6-311++G(d,p)			B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν_{cal}	a_{IR}	b_{Raman}	ν_{cal}	a_{IR}	b_{Raman}	
1			4	0.073	0.000	4	0.007	1.850	ω (CH ₂ of CH ₃)
2			5	0.009	0.000	7	0.024	1.497	ω (CH ₃)
3			8	0.000	1.784	10	0.014	1.514	γ (CH)
4			14	0.515	0.000	17	0.158	2.596	γ (CH)
5			14	0.000	1.635	23	1.561	1.472	γ (CH)
6			25	1.369	0.000	25	2.025	2.205	γ (CH)+ ω (CH ₂ of CH ₃)
7			27	0.000	5.896	32	0.385	3.210	ω (C=O)+ γ (CH)
8			33	2.848	0.000	41	0.403	2.619	ω (C=O)+ γ (CH)
9			40	0.000	1.742	42	0.943	1.027	γ (CH)
10			49	4.489	0.000	48	1.979	1.188	(C-O) Stretching
11			52	0.000	1.578	52	0.210	2.066	γ (CH)+ ω (CH ₂ of CH ₃)
12			63	0.000	1.589	74	2.773	1.080	ω (CH ₃)
13			67	8.037	0.000	80	5.642	0.660	ω (CH ₃)
14			79	0.000	1.373	88	3.396	0.630	ω (CH ₂)
15			89	10.872	0.000	94	0.628	1.003	CH ₂
16			99	0.000	1.558	111	1.907	1.210	CH ₂
17			112	8.327	0.000	112	5.846	0.260	CH ₂
18			114	7.653	0.000	118	6.499	0.067	CH ₂
19			134	15.689	0.000	131	5.472	0.328	ω (CH ₃)
20			138	0.000	0.272	139	17.142	0.208	ω [(CH ₃)+NH ₃]
21			182	0.000	0.315	167	1.166	0.568	ω [(CH ₃)+NH ₃]

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	FT-IR	Raman	ν_{cal}	a_{IR}	b_{IR} Raman	ν_{cal}	a_{IR}	b_{IR} Raman	
22			194	17.858	0.000	201	41.528	1.642	t(CH ₃)
23			208	0.000	4.753	219	6.370	4.839	t(CH ₃)
24			244	9.146	0.000	230	4.060	0.741	t(CH ₃)
25			244	0.000	0.817	232	2.624	1.107	ω [(CH ₃)+NH ₃]
26			270	0.002	0.483	247	6.051	0.350	t(CH ₃)
27			270	1.191	0.001	249	1.459	0.360	t(CH ₃)
28			339	0.000	6.554	318	0.109	4.549	C-C
29			347	20.339	0.000	339	22.406	0.395	ω (NH ₃)
30			357	0.000	2.011	352	8.204	4.904	ω (NH ₃)
31			373	4.900	0.000	355	3.068	0.915	ω (NH ₃)
32			404	5.530	0.001	374	3.324	3.044	ω (NH ₃)+ γ (CH)
33			404	0.001	5.149	376	1.925	1.961	ω (NH ₃)+ γ (CH)
34			426	0.000	3.077	417	0.172	2.061	γ (CH)+(NH ₃)
35			428	17.392	0.000	418	4.609	0.682	γ (CH)
36			463	0.000	5.304	429	0.376	2.620	γ (CH)
37			463	2.651	0.000	429	0.890	2.605	t(NH ₃)+(CH)
38			467	0.000	1.891	438	2.480	1.497	t(NH ₃)+(CH)
39			468	15.393	0.000	445	41.174	0.603	ω (NH ₃)
40			487	19.421	0.000	473	8.356	0.445	t(NH ₃)
41	513		489	0.000	0.802	475	7.597	0.529	t(NH ₃)
42			569	0.570	3.081	525	38.728	0.572	t(NH ₃)
43			569	5.809	0.302	526	16.399	1.184	γ (CH)
44			580	69.983	0.000	536	4.442	1.229	γ (CH)
45			580	0.000	0.726	536	5.449	1.175	β (CH)+ ρ (CH ₃)
46	621		663	70.342	0.000	620	22.129	0.336	β (CH)+ ρ (CH ₃)
47			695	0.000	4.309	651	2.742	7.484	C=O Vibration
48			701	0.636	0.000	655	0.227	6.484	ρ (CH ₂)
49			701	0.000	12.489	656	1.054	4.551	β (CH) +Ring deformation
50	117	751	777	0.000	2.534	717	23.932	5.343	β (CH)+ Ring deformation
51			779	135.974	0.000	720	12.365	1.935	γ (CH) +(NH ₃)
52			787	0.000	4.919	723	2.747	3.499	γ (CH) +(NH ₃)

Mode Number	Experimental		HF/6-311++G(d,p)			B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν_{cal}	a_1^{IR}	b_1^{Raman}	ν_{cal}	a_1^{IR}	b_1^{Raman}	
53			787	55.744	0.000	736	97.797	2.265	γ (CH)
54	781		788	0.000	3.444	736	76.996	1.395	ν (C=N+C=O)
55			792	0.936	0.000	746	2.790	1.311	ν C-N + Ring breath
56			818	19.527	0.000	751	7.940	0.620	(C-H)
57			857	0.000	1.714	803	1.392	0.181	(C-H)
58			882	30.791	0.001	808	3.833	0.994	γ (CH)
59			884	0.003	9.796	810	7.023	1.392	γ (CH)
60			906	1.990	0.027	823	48.722	3.324	γ (H)+(NH ₃)
61			906	0.001	75.846	824	38.482	3.277	ρ (H ₂)+(H)
62			915	1.297	0.000	844	72.960	5.907	C-H +Ring breath
63			915	0.000	1.744	844	7.509	59.577	C-H +Ring breath
64			948	184.126	0.000	883	466.583	22.205	ρ (NH ₃)
65		947	949	0.022	1.076	886	158.098	41.891	ρ (NH ₃)
66			975	44.822	0.000	903	31.353	1.189	ν C-C
67			978	0.001	4.774	904	14.994	4.661	C-H
68	947		991	771.395	0.006	929	2.461	1.171	C-H
69			993	0.221	19.909	934	46.091	2.189	γ (CH)+(NH ₃)
70			1010	71.800	0.000	936	33.831	3.201	γ (CH)
71			1049	40.681	0.001	953	0.139	0.030	γ (CH)
72			1049	0.022	1.524	954	0.267	0.037	γ (CH)
73			1077	0.095	0.180	1013	67.170	5.939	(C-C) + (O-H)
74			1077	0.708	0.024	1018	76.956	8.264	ρ (OH)
75			1086	1.795	0.000	1020	82.708	11.123	β (O-H)
76			1098	8.478	0.001	1025	27.417	1.865	β (CH)+(O-H)
77	1033		1098	0.017	0.523	1025	43.545	6.374	β (CH)+(O-H)
78			1122	0.000	9.431	1053	2.931	4.929	O-H+ β (CH)
79			1148	0.000	29.224	1063	66.419	15.085	C-O+ β (CH)
80	1152		1160	53.116	1.585	1063	18.039	6.113	β (CH)
81			1160	43.999	1.912	1064	35.678	16.137	ρ (CH ₂)
82			1179	67.927	0.362	1088	43.372	1.749	ω (CH ₂)

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	FT-IR	Raman	ν_{cal}	a_{IR}	b_{IR} Raman	ν_{cal}	a_{IR}	b_{IR} Raman	
83			1179	1.916	12.859	1108	10.588	1.826	β (CH)+ ρ (NH ₃)
84			1189	0.000	3.815	1110	11.549	1.433	β (CH)+ ρ (NH ₃)
85			1193	24.588	0.000	1141	58.235	2.314	(CH ₂)
86			1194	0.000	2.689	1156	5.561	0.668	(CH)+ ρ (NH ₃)
87			1232	106.100	0.000	1156	6.178	1.418	(CH)+ ρ (NH ₃)
88	1271		1279	0.236	4.674	1168	0.679	2.637	ω (CH ₃)
89			1279	4.966	0.222	1168	0.702	2.738	ω (CH ₃)
90			1286	3.415	2.679	1196	8.230	7.445	β (CH)
91			1286	1.127	8.122	1196	6.936	8.434	Strong β (CH)
92			1303	0.003	13.559	1202	10.751	6.203	ω (CH ₃)+(CH)
93			1303	12.081	0.003	1202	13.082	7.550	ω (CH ₃)
94		w 1320	1328	0.046	8.863	1245	164.196	4.232	ρ (CH ₂)
95			1328	59.677	0.007	1255	76.441	0.563	ρ (CH ₂)
96			1353	0.000	6.411	1259	301.662	7.413	β (CH)+(NH ₃)
97			1355	38.517	0.000	1260	149.752	1.654	β (CH)
98			1357	251.193	0.001	1276	105.532	44.217	ν C-O + Ring vibration
99			1358	0.012	22.574	1277	43.993	5.710	ν C-O + Ring vibration+(NH ₃)
100	1363		1404	427.649	0.000	1288	91.300	5.260	(C-H)
101			1415	0.004	53.562	1310	295.112	1.510	(C-H)
102		w 1418	1416	464.116	0.000	1327	29.720	1.262	(C-H)
103			1420	0.000	4.354	1332	12.509	7.436	β (CH)
104			1442	154.339	0.000	1333	13.717	5.896	β (CH)
105			1445	0.000	7.582	1335	47.639	3.602	β (CH)
106			1447	0.000	10.028	1336	19.940	13.315	ω (CH ₂)
107			1460	22.383	0.000	1362	15.610	2.465	(CH)+ ω (NH ₃)+Ring breathing
108		1445	1460	0.000	4.158	1363	33.978	14.182	β (CH)+ ω (NH ₃)
109			1503	1.779	0.000	1374	17.383	0.067	ω (CH ₂)
110			1540	0.000	5.275	1397	0.219	3.101	ω (CH ₂)
111	1525		1548	149.853	0.000	1456	32.186	2.929	C=C
112			1552	0.000	3.778	1457	12.746	16.474	C-N
113			1587	0.478	1.223	1471	2.205	1.168	C-C

Mode Number	Experimental		HF/6-311++G(d,p)			B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν_{cal}	a_{IR}	b_{Raman}	ν_{cal}	a_{IR}	b_{Raman}	
114	1593		1587	0.450	1.299	1471	1.981	1.666	ω (CH ₃)+ β (CH)+ ω (NH ₃)
115			1603	21.928	0.000	1476	11.669	2.908	β (CH)+ ρ (NH ₃)+Ring breathing
116			1605	44.358	0.001	1476	9.470	3.173	ω (CH ₃)
117			1605	0.007	5.419	1478	10.746	0.372	ω (CH ₃)
118			1607	0.000	28.806	1482	3.339	35.459	ω (CH ₂)
119			1617	0.000	10.077	1492	8.944	13.945	ρ (CH ₂)
120			1620	4.413	17.587	1492	9.052	13.736	ρ (CH ₃)
121			1620	10.841	7.160	1495	0.174	10.993	ω (CH ₃)
122			1630	56.895	0.003	1506	39.835	4.844	ω (CH ₂)
123	m1635		1631	0.014	11.487	1506	43.941	4.742	δ (CH ₃)
124			1631	14.605	0.000	1512	12.766	0.050	δ (CH ₃)
125			1676	565.120	0.000	1544	230.827	2.262	(C-H) + ρ (CH ₂)
126			1676	0.003	1.091	1544	289.154	1.040	ρ (NH ₃)+Ring breathing
127			1776	12.214	0.069	1629	5.050	7.455	Ring breathing
128		w 2612	1776	0.054	15.743	1629	4.342	7.269	ρ (NH ₃)+C=C, C-C+vC-H
129			1798	3.893	14.276	1659	19.584	51.498	δ (NH ₃) + Ring vibration
130			1798	125.368	0.444	1659	18.391	50.961	δ (NH ₃) + Ring vibration
131			1817	0.012	90.301	1668	32.382	37.671	δ (NH ₃)
132			1817	17.828	0.060	1670	36.747	29.436	δ (NH ₃)
133	1950		1959	923.306	0.000	1763	292.659	4.785	ν C=O+ ω (OH)
134	w2349	s 2816	1962	0.001	17.331	1767	370.950	33.482	ν C=O+ ω (OH)
135	2760	s 2919	3158	0.000	141.895	2999	51.195	134.252	γ O-H
136	2864		3159	34.562	195.989	2999	68.753	210.806	ν_s CH ₃
137			3159	74.886	90.357	3017	3.666	209.255	ν_{as} CH ₂
138			3166	36.716	0.000	3021	16.272	34.428	ν_{as} CH ₂
139	2987	s3024	3192	0.009	109.860	3040	3.148	97.353	N...O-H
140			3195	46.340	0.018	3043	35.288	10.835	ν C-H
141			3201	0.001	132.670	3054	3.251	80.730	ν C-H
142		s2923	3216	16.925	69.247	3056	41.208	61.295	ν_{as} CH ₂
143			3216	87.985	13.320	3056	40.453	58.026	ν_{as} CH ₂ of CH ₃

Mode Number	Experimental		HF/6-311++G(d,p)			B3LYP/6-311++G(d,p)			Assignment
	FT-IR	Raman	ν_{cal}	a_{IR}	b_{I} Raman	ν_{cal}	a_{IR}	b_{I} Raman	
144	w3132		3219	20.287	0.000	3073	14.552	28.178	ν_{as} CH ₂
145			3257	0.000	58.877	3104	36.892	50.835	ν C-H
146			3261	59.232	0.000	3107	41.377	22.661	ν C-H
147			3279	87.547	0.368	3131	31.170	137.568	ν_{as} CH ₃
148			3279	0.121	265.626	3131	29.688	132.155	ν_{as} CH ₃
149			3316	4.326	118.040	3159	659.126	65.583	ν_{as} C-H
150			3316	28.037	18.210	3160	952.960	101.221	ν (C-H+O-H)
151	3242		3326	13.626	30.481	3161	2616.119	107.871	ν (C-H+O-H)
152			3326	4.625	89.802	3166	186.311	1199.658	ν O-H
153			3353	11.653	54.436	3167	10.025	93.623	ν O-H
154			3353	3.186	199.023	3167	12.584	95.507	ν C-H
155	3255w		3366	4.204	121.356	3193	2.483	160.586	ν C-H
156			3366	12.765	39.969	3193	2.415	160.045	ν C-H
157	w3323		3740	21.741	117.941	3204	5.737	88.618	ν C=H
158			3740	16.538	155.017	3205	5.607	92.225	ν N-H
159			3823	2192.191	0.132	3486	71.280	163.555	ν_s (NH ₃)
160			3825	0.574	491.344	3487	62.528	182.745	ν_{as} (NH ₃)
161			3831	191.489	2.756	3585	30.563	60.052	ν_{as} (NH ₃)
162			3831	5.307	101.720	3585	29.324	66.855	ν_{as} (NH ₃)

Generally, the N–H stretching vibrations occur in the region of 3600–3300 cm⁻¹ in amines. In the present study, N–H symmetric stretching mode is assigned at 3888 cm⁻¹ in FT-IR and inactive in Raman spectrum. In this compound, each of the N-H bond of the (NH₃)⁺ group is hydrogen bonded with the oxygen atom of the adipate anion. In 4MAA an intense peak calculated at 3831 and 3585 cm⁻¹ in HF and DFT/B3LYP methods respectively, are assigned to NH₃⁺ asymmetric mode. The rocking vibration of NH₃⁺ group is observed at 1676 and 1544 cm⁻¹ in HF and DFT/B3LYP calculations respectively whereas the corresponding experimental IR and Raman bands were absent. The NH₃⁺ wagging vibration is observed in IR at 1593 cm⁻¹ and in Raman spectrum it is absent.

Vibrations of N-H...O

The intermolecular hydrogen bond was formed between amine N atom and carbonyl O atom after optimization. The present structure has N-H...O bond of cation, which is observed as medium peak at 3024 cm⁻¹ in Raman spectrum and inactive in IR spectrum. This band is theoretically calculated at 3192 cm⁻¹ and 3040 cm⁻¹ HF and B3LYP

methods, respectively. The stretching vibration of this N–H...O hydrogen bond interactions is proved and it is good correlation with the theoretical calculations.

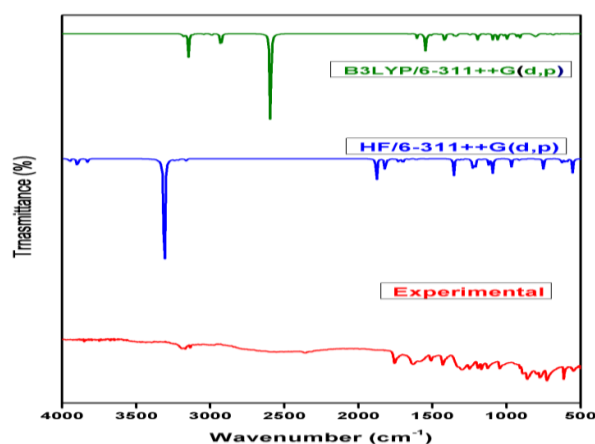


Fig. 6. FT-IR spectra for 4MAA

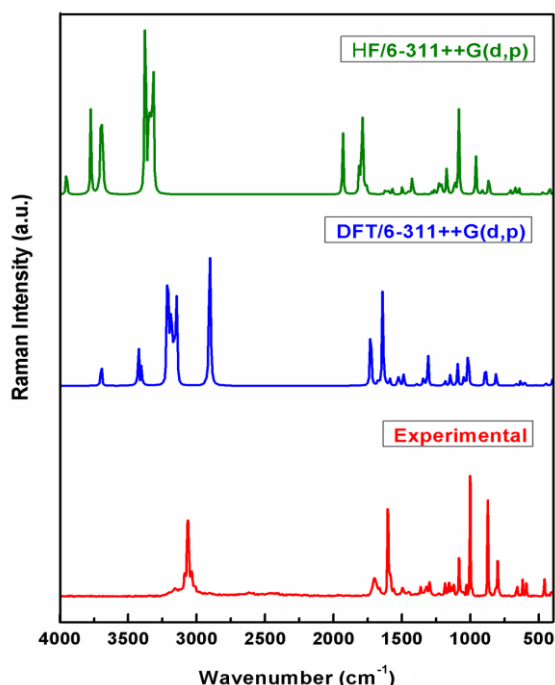


Fig. 7. FT-Raman spectra for 4MAA

D. Nonlinear optical behaviour

Nonlinear optics is at the forefront of current research because of its significance in provided that the key functions of frequency conversion, optical limiter and optical data storage devices for the emerging technologies. Non linear optical parameters such as dipole moment (μ), polarizability (α), first-order hyperpolarizability (β) and second order hyperpolarizability (γ) were calculated at the B3LYP methods with 6-311++G(d,p) levels and the calculated values are reported in Table IV. Therefore, the second order hyperpolarizability calculation [9-11] was attempted and the second order hyperpolarizability value is comparably 74 times greater than the urea (4.728×10^{-36} esu). These above results show that the present molecule is excellent material for optoelectronic applications

Table IV: Non linear optical parameters of 4MAA calculated by DFT/B3LYP with 6-311++G(d,p) levels

Parameter	a.u	esu ($\times 10^{-24}$)	Parameter	a.u	esu ($\times 10^{-33}$)	Parameter	a.u	esu (10^{-36})
μ_x	-0.0102		β_{xxx}	-0.0375	-0.33146	γ_{xxxx}	282531.9	262.469
μ_y	0.0040		β_{xxy}	-0.0054	-0.04773	γ_{xxyy}	99379.29	114.323
μ_z	0.0024		β_{xyy}	-0.0202	-0.17855	γ_{yyyy}	586289	101.346
μ	0.0112		β_{yyy}	-0.0002	-0.00177	γ_{yyzz}	582984.2	237.619
α_{xx}	-0.7528	-0.11156	β_{xxz}	0.0166	0.146727	γ_{xxzz}	65192.57	128.441
α_{xy}	-27.6109	-4.09194	β_{xyz}	0.0073	0.064525	γ_{zzzz}	145979.6	441.0920
α_{yy}	-125.0021	-18.5253	β_{yyz}	-0.0015	-0.01326	γ	501983	353.135
α_{xz}	30.9564	4.587738	β_{xzz}	-0.0027	-0.02387			
α_{yz}	-30.5133	-4.52207	β_{yzz}	-0.0015	-0.01326			
α_{zz}	-179.8625	-26.6556	β_{zzz}	0.0023	0.02033			
α	-101.8724	-15.0974	β_0	0.06326	0.05591			
$\Delta\alpha$	356.8715	52.8883						

III. CONCLUSION

The optimized geometrical parameters, NLO properties, electronic properties and vibrational assignments of the 4MAA have been studied by HF and DFT calculations. The complete theoretical and experimental vibrational assignments were analyzed as well as compared. The good agreement of the calculated and observed vibrational spectra reveals the advantages of higher basis sets for computational calculations. The FMOs energies show that charge transfer occurs within the molecule. The title compounds exhibited good NLO property and were much 74 times higher than that of reference urea.

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